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Quantitative Analysis of Charge Injection and Discharging of Si Nanocrystals and Arrays by Electrostatic Force Microscopy

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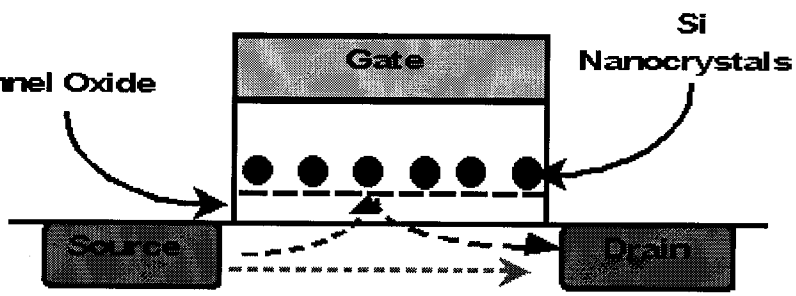
Introduction / Background

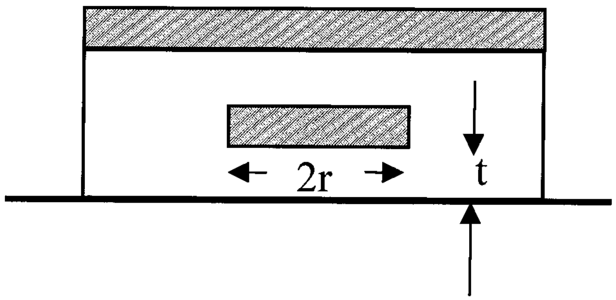
- NASA requirements for computing and memory for microspacecraft emphasize high density, low power, small size, and radiation hardness.
- The distributed nature of a storage elements in nanocrystal floating-gate memories leads to intrinsic fault tolerance and radiation-hardness. Conventional floating-gate non-volatile memories are more susceptible to radiation damage.
- Nanocrystal-based memories also offer the possibility of faster, lower power operation.



- **Write**: electrons tunnel from substrate channel into nanocrystal storage nodes.
- **Non-destructive readout**: performed by sensing the field from the stored charge.

Why Small Is Good

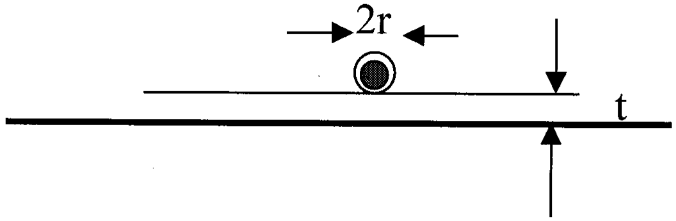
GaAs/AlGaAs Dual gate device
(e-beam lithography)



t = 5-25 nm
r = 25-50 nm
C = 1-10 fF
$\Delta E_{1e-} = e^2/2C$ = 0.05-0.5 meV

at 300K, kT = 26 meV

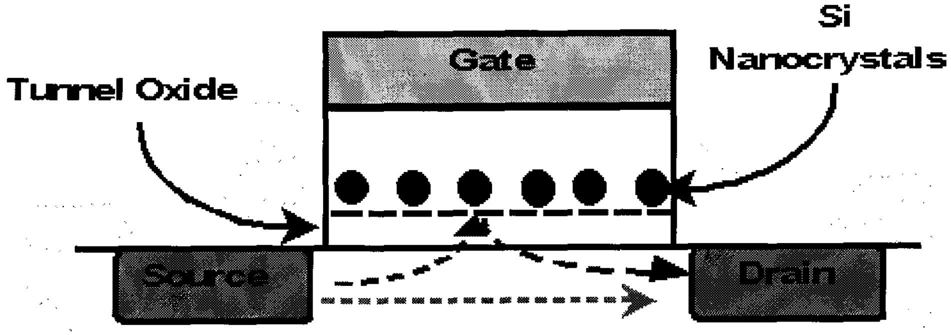
Size-classified Si nanoparticle on SiO_2



t = 2-5 nm
r = 2-5 nm
C = 1-10 aF
$\Delta E_{1e-} = e^2/2C$ = 50-500 meV

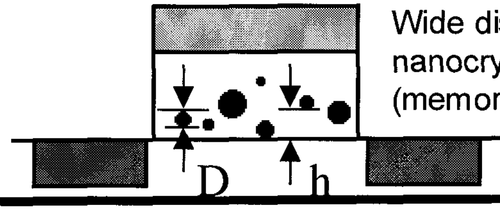
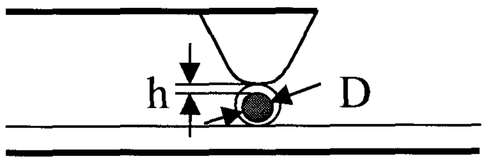
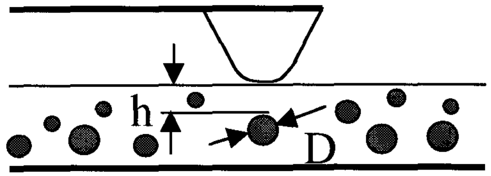
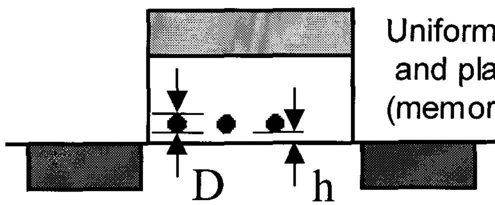
Si nanocrystal memories may enable room-temperature sensing of single-electron storage

State of the Art



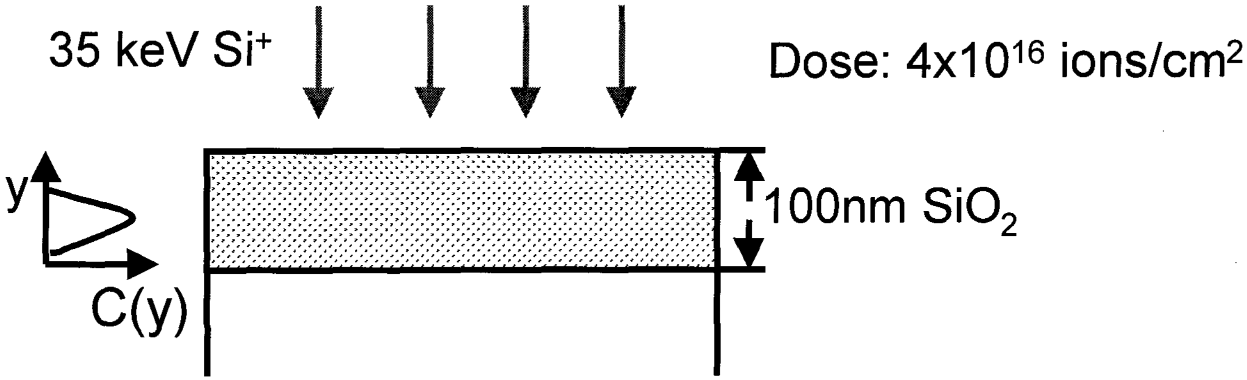
Advantages of a nanocrystal floating gate:

- thin tunnel oxide - fast
- small nanocrystal size - lower power
- isolated nanocrystal floating gates - greater reliability

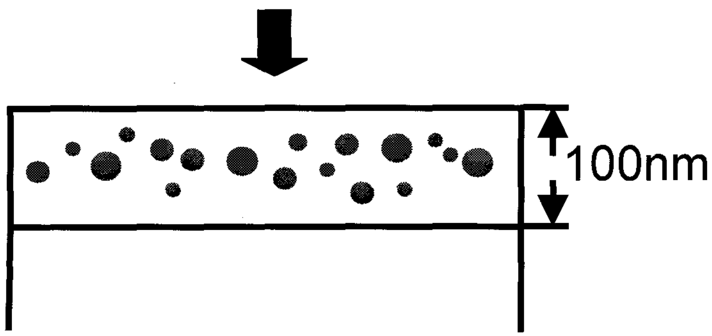
Previous work: (Tiwari, IBM)	 Wide distribution of nanocrystal size and placement (memory element non-uniformity)
Single-particle addressing by AFM	 
Future goal: uniform nc ensembles	 Uniform nanocrystal size and placement (memory element uniformity)

Si Nanocrystal Synthesis by Implantation

Ion implantation



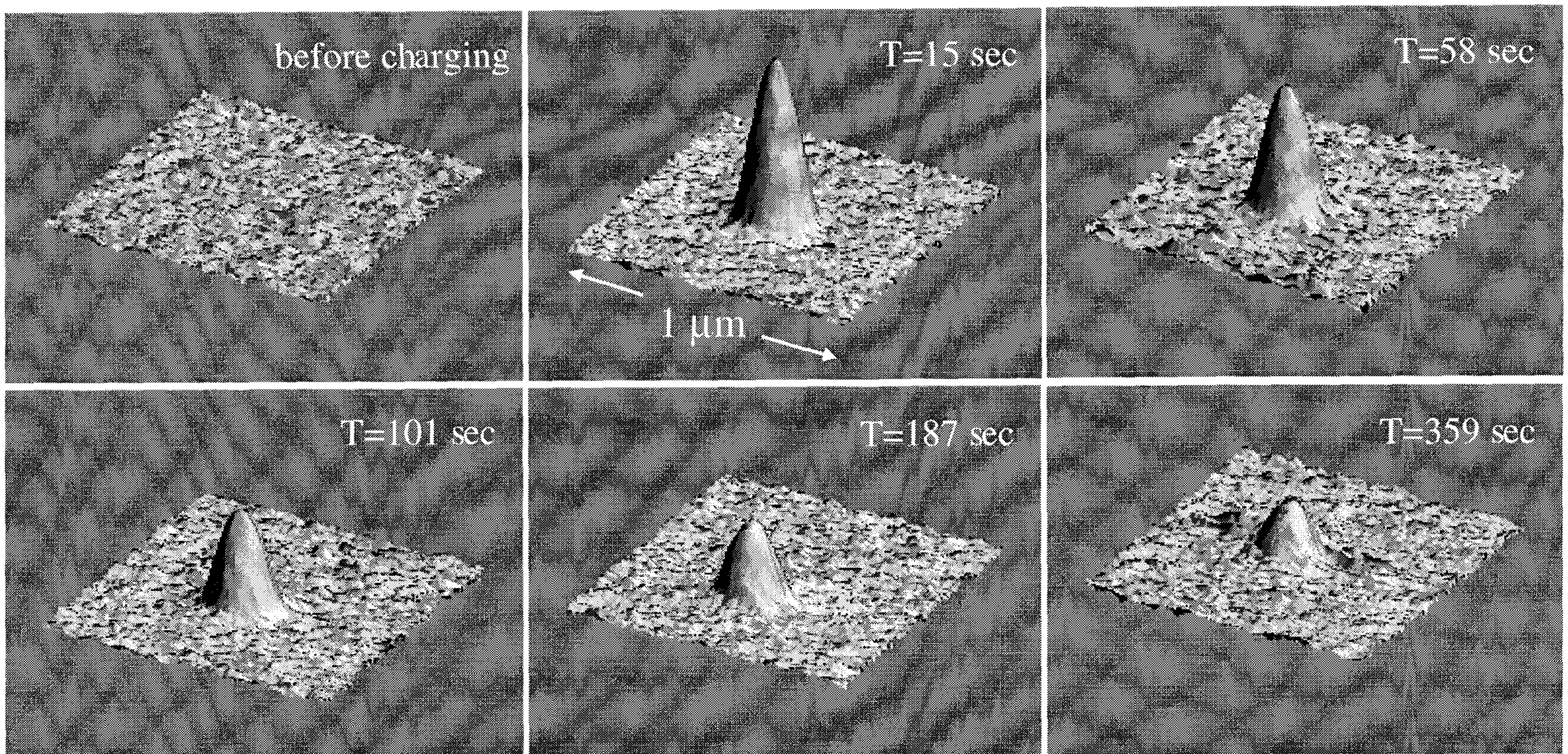
Vacuum anneal 1100°C, 10 minutes



K.S. Min et al. *Appl. Phys.Lett.* **68**, 2511 (1996)

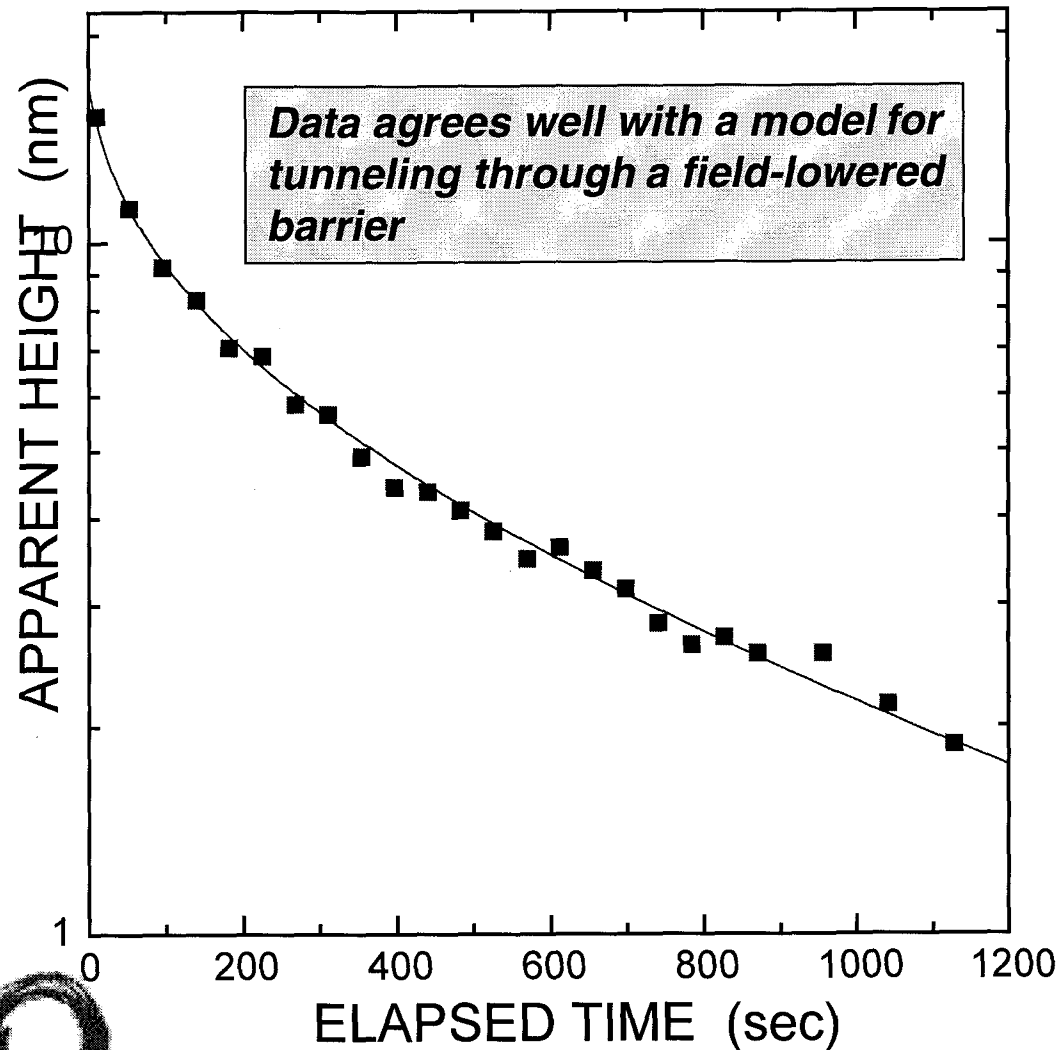
Charging of Ion-implanted Si Nanocrystals

- Apparent height of charged area ranges from 11.2 nm to 4.4 nm.
- Significance: Charging / discharging can be seen. Individual memory element operation can be simulated and observed.



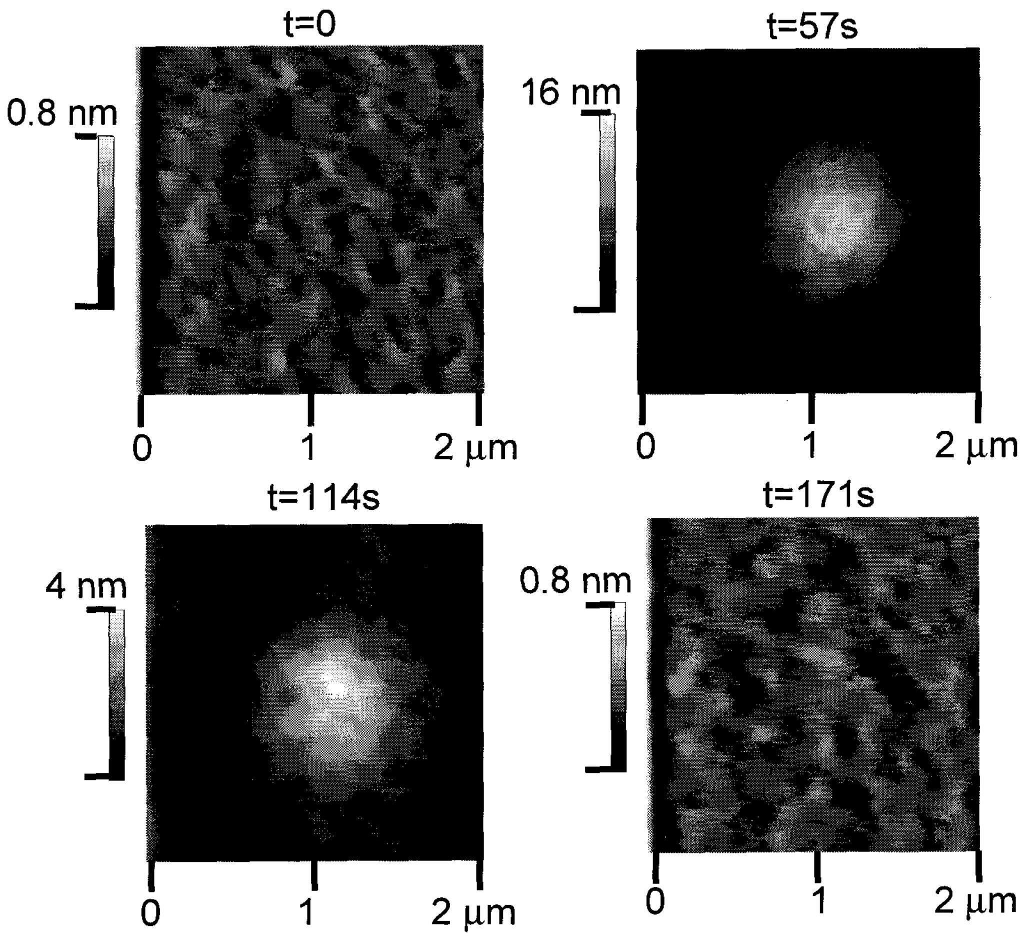
Nanocrystal charging/discharging can be ***imaged***

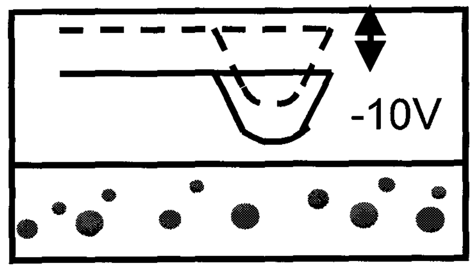
Charging of Ion-implanted Si Nanocrystals



- AFM measurements can be used to track and quantify the slow discharge of a nanocrystals implanted within an oxide layer.
- Charging is measured by the AFM tip as a *localized apparent height change.*

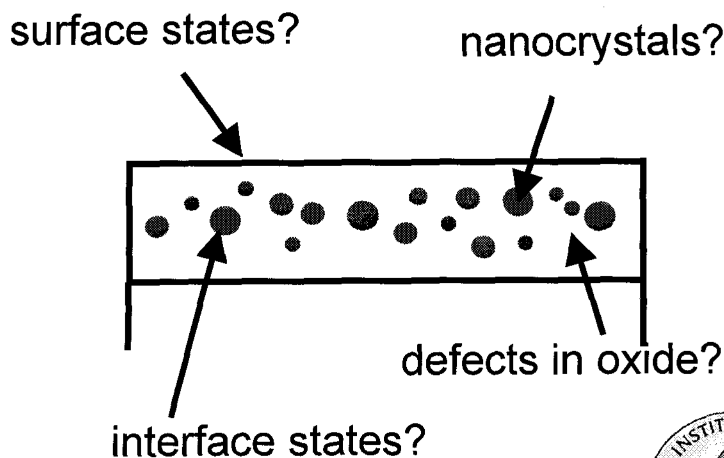
Charging of Ion Implanted Samples





4×10^{16} at/cm^2, annealed 1100°C, 10 minutes

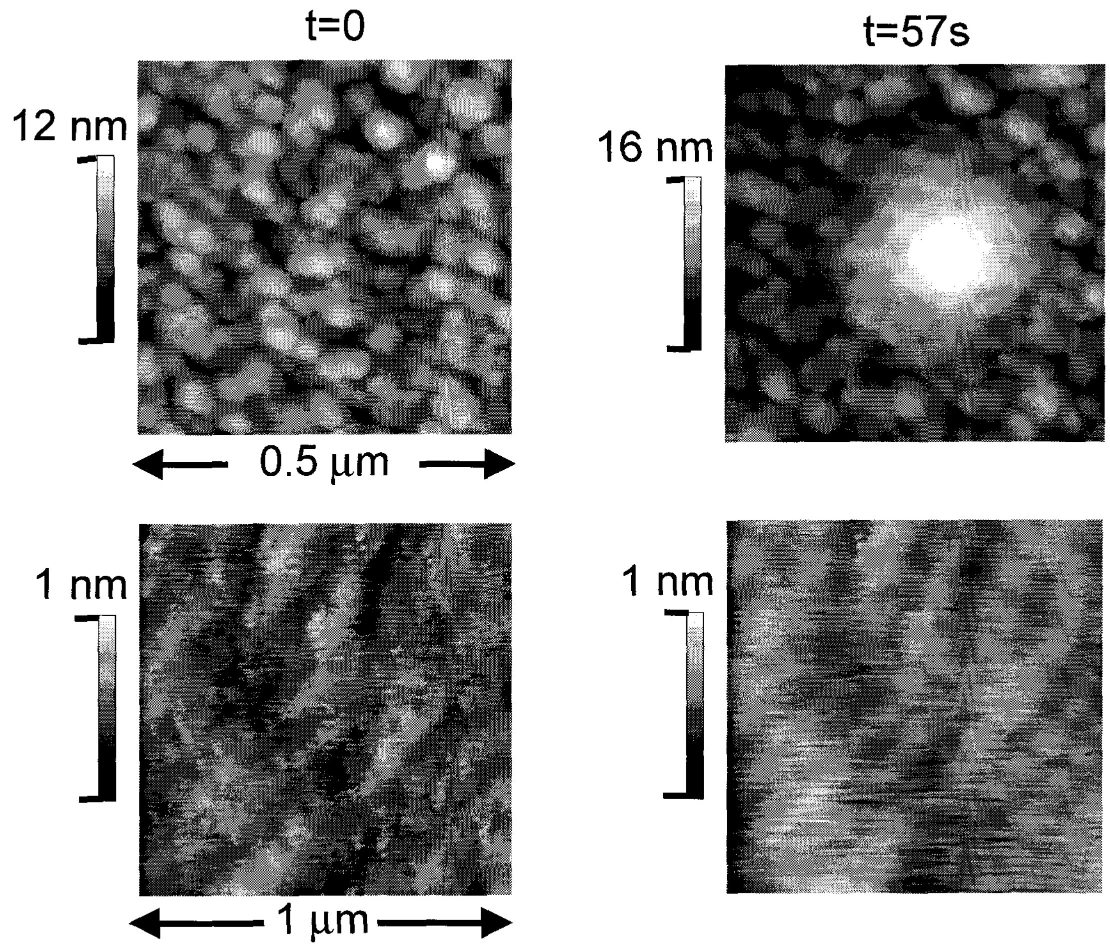
Where is the charge stored?



Is Charge Stored in Nanoparticle Floating Gate or Oxide Defects?

Ion-implanted Si nanoparticle floating gate material:
Stores Charge

Similar oxide, no Si nanoparticles, but ion-damaged by Ar^+ implantation:
No Measurable Charge Storage

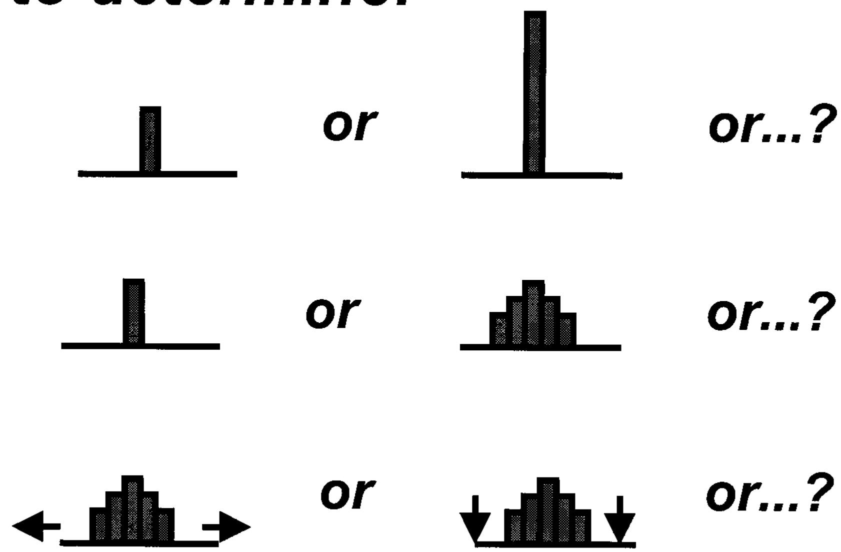


Locus of Charge Storage is Si Nanoparticle Floating Gate, Not Oxide Defects

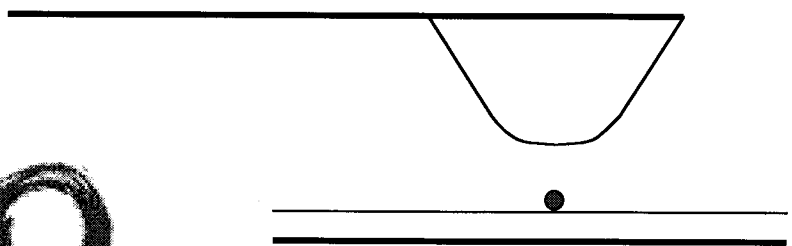
Interpretation of Charging Data

What we want to determine:

- How much charge is stored?
- Distribution of charge?
- Dissipation of charge?

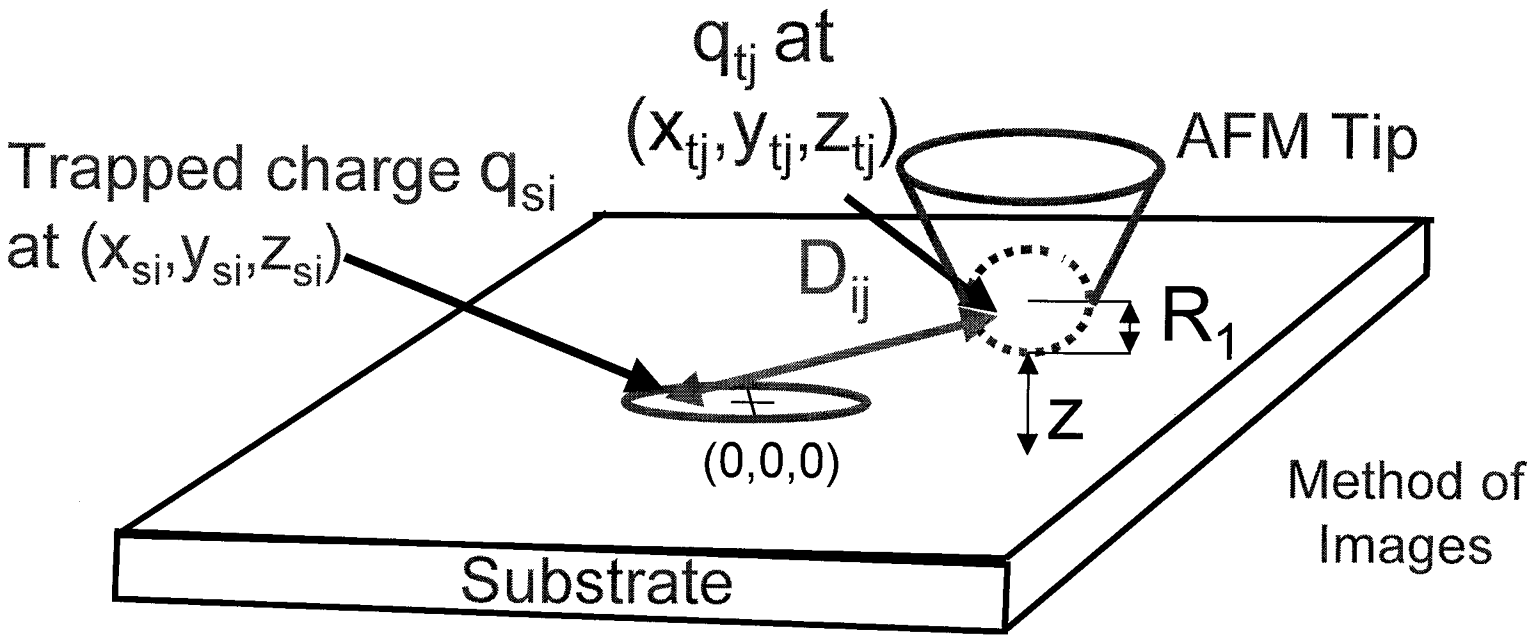


Model requirements:



- Tip-sample convolution
- Tip-charge interaction vs. normal AFM operation

Model: AFM Tip-Charge Distribution Interaction



$$D_{ij}^2 = (z_{s_i} - z_{t_j})^2 + (x_{s_i} - x_{t_j})^2 + (y_{s_i} - y_{t_j})^2$$

Coulomb interaction between q_{si} and q_{tj}:

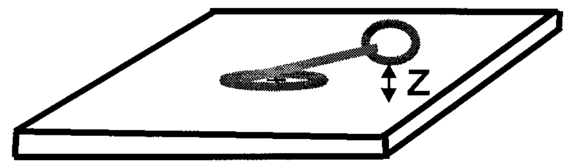
$$\boxed{\vec{F}_{ij} = \frac{q_{s_i} * q_{t_j}}{4\pi\varepsilon_o D_{ij}^2}\hat{d}_{ij}}$$

Non-Contact AFM Maps Height at Constant Force Gradient

Coulomb interaction between q_{si} and q_{tj}:

$$\boxed{\vec{F}_{ij} = \frac{q_{s_i} * q_{t_j}}{4\pi\varepsilon_o D_{ij}^2}\hat{d}_{ij}}$$

Find z-component of electrostatic force; differentiate by z:

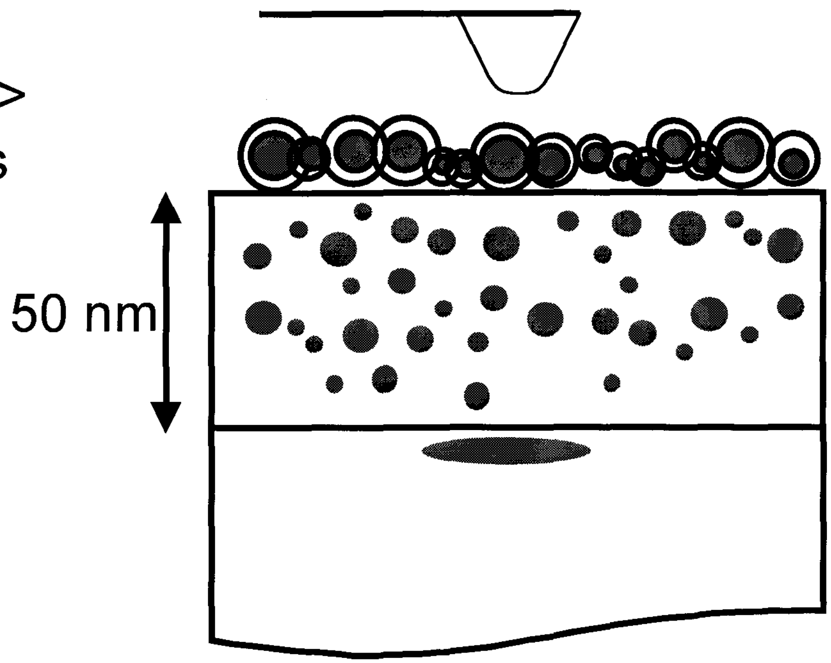


Finally, total force gradient is sum of electrostatic and Van der Waals interactions

$$\boxed{\left(\frac{\partial F_z}{\partial z}\right)_{tot} = \left(\frac{\partial F_z}{\partial z}\right)_{vdW} + \sum_{i,j}\left(\frac{\partial F_z}{\partial z}\right)_{ij} = \text{const}}$$

Some Assumptions: Buried NC Charging

- Charge distribution: uniform, coarse grid, only on surface -- appropriate for these samples
- Neglect image charge in substrate --> Good approximation due to distances involved
- Neglect topography
- Neglect effect of hydrodynamic damping
- Assume tip is not "tapping" the surface--valid for a limited operating range



Quantitative Nanoscale Charge Imaging

Experimental EFM Image of Charged Si Nanoparticle Floating Gate:

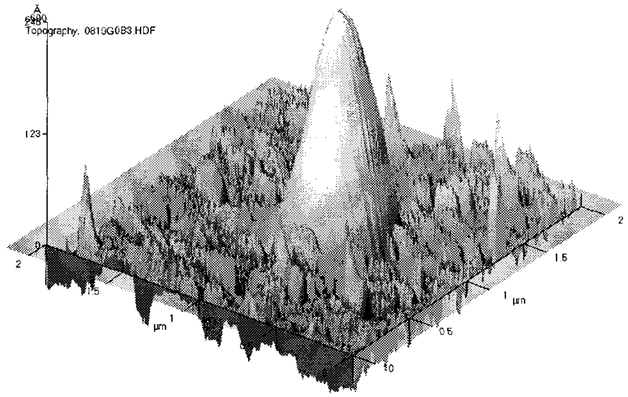
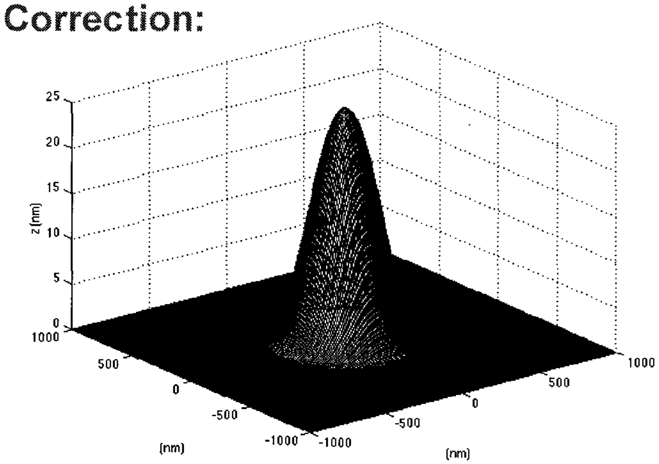
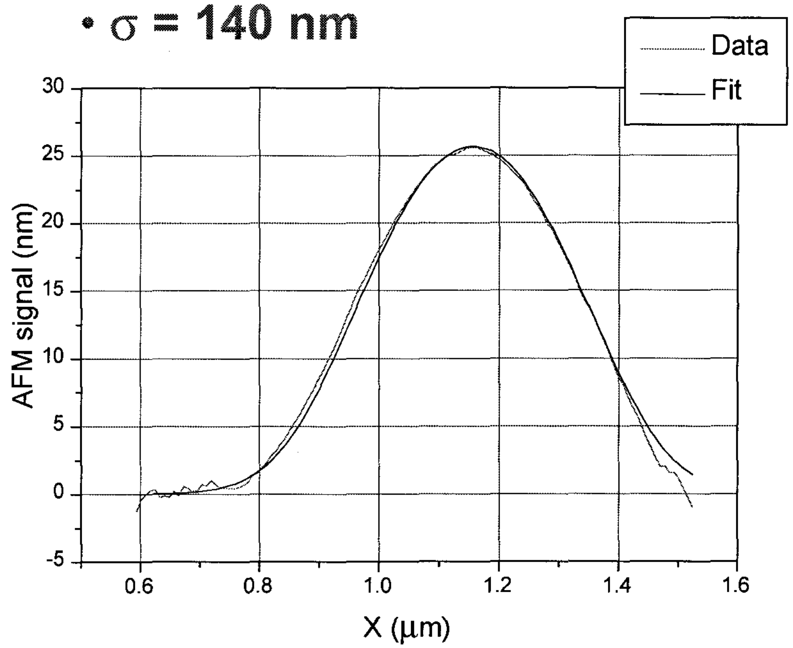


Image Simulation (w/ Tip Convolution Correction:



Fit results:

- total charge = 200 electrons
- σ = 140 nm



Amount of stored charge can be determined

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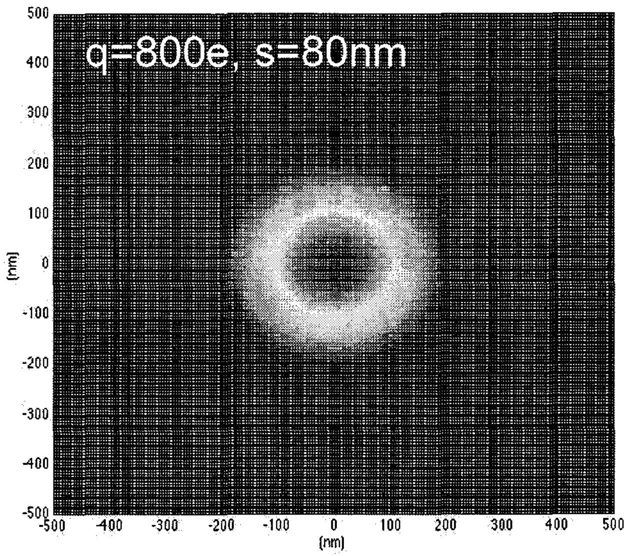
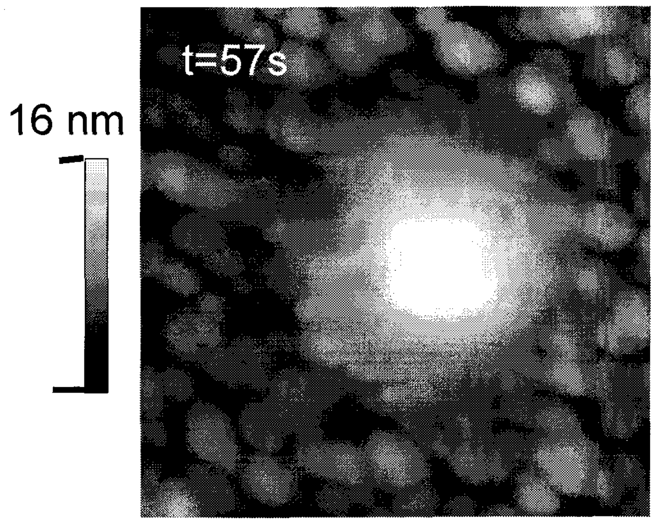
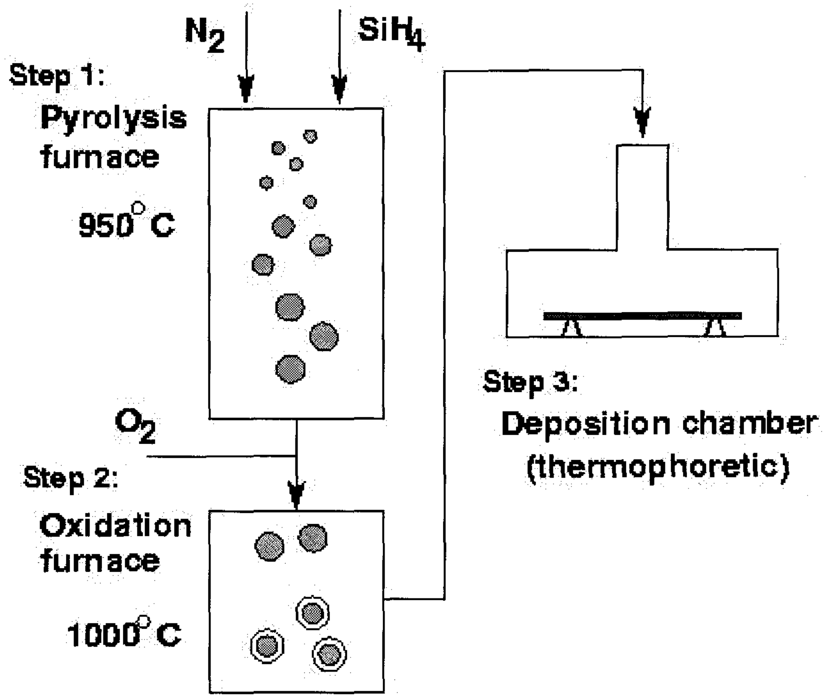
Goal of electrostatic modeling

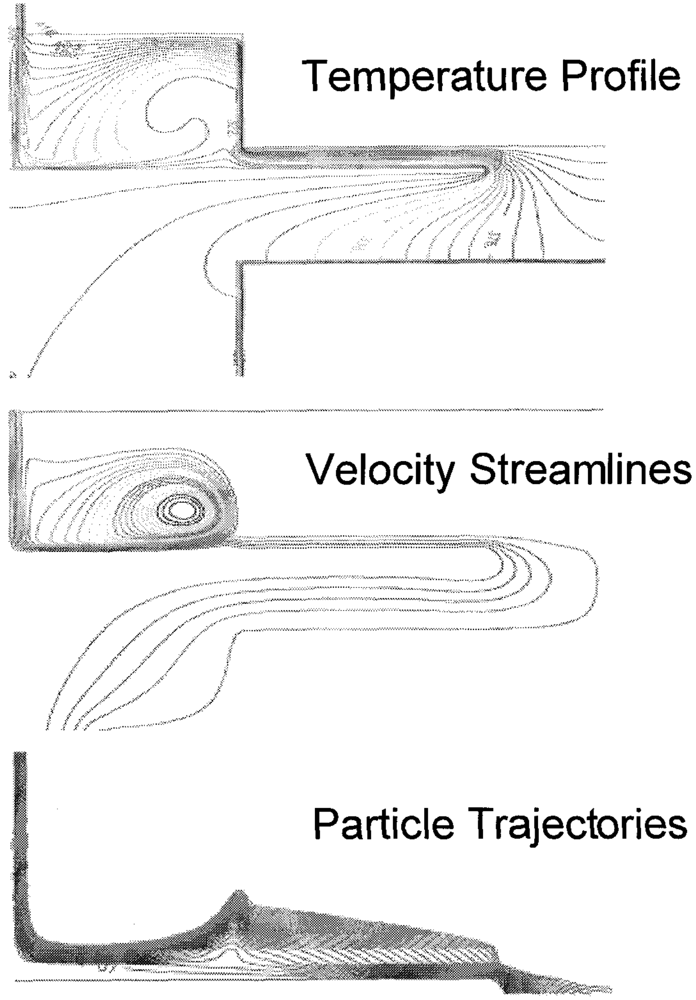
- Calculated "images" qualitatively match experimental results
- Quantitative comparison will allow the amount of charge deposited, charge distribution and discharging mechanism to be determined from AFM images





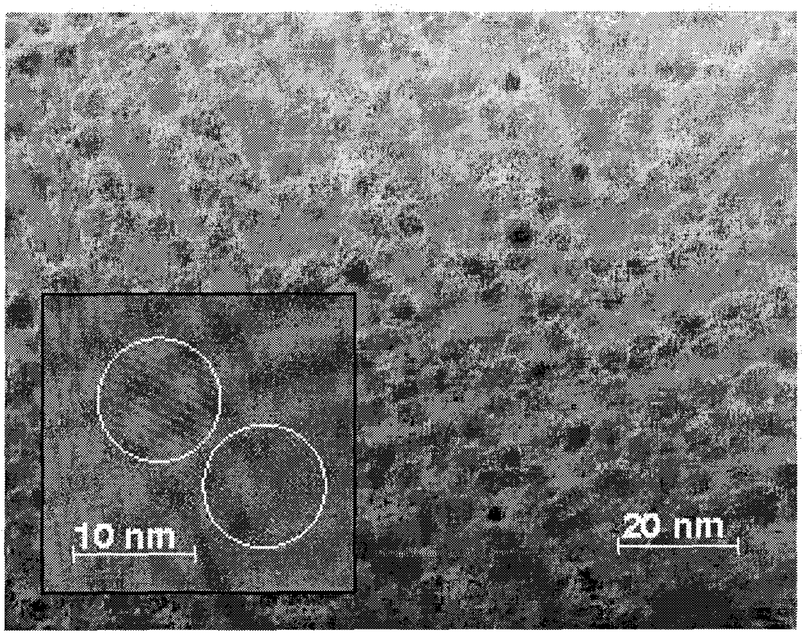
Aerosol Synthesis of Si Nanocrystals





Aerosol synthesis and thermophoretic deposition can produce uniform layers of Si nanocrystals.

Nanocrystal Deposition



Planar view TEM of an aerosol nanocrystal monolayer.

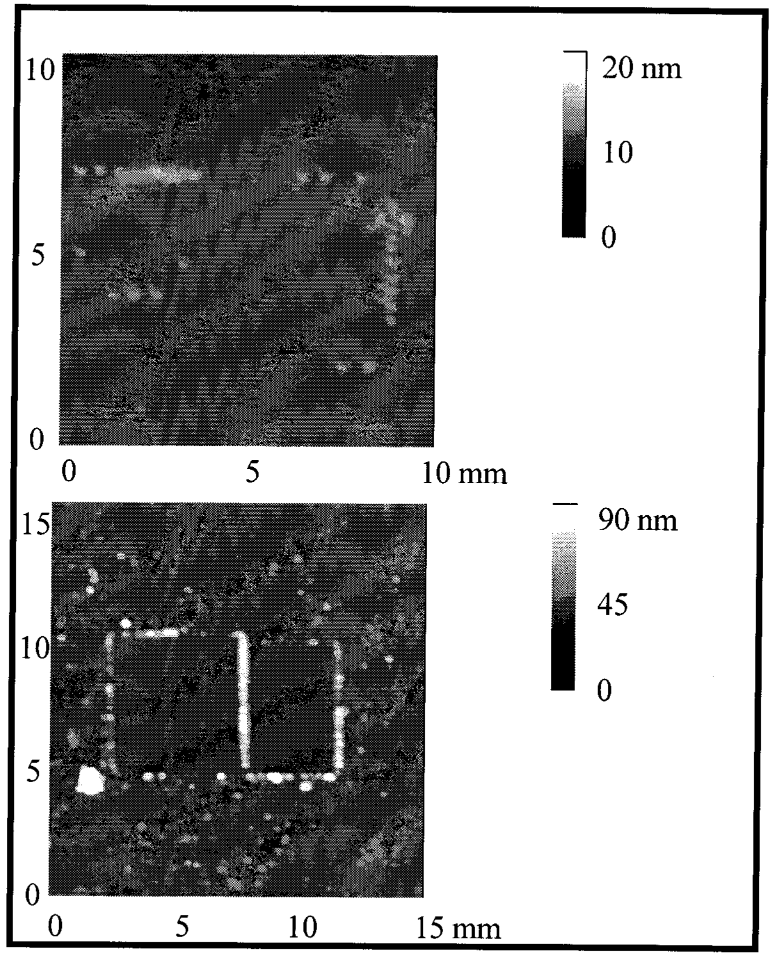
Crystal size = 4-5nm

Particle density = $6x10^{12}$ cm^{-2}

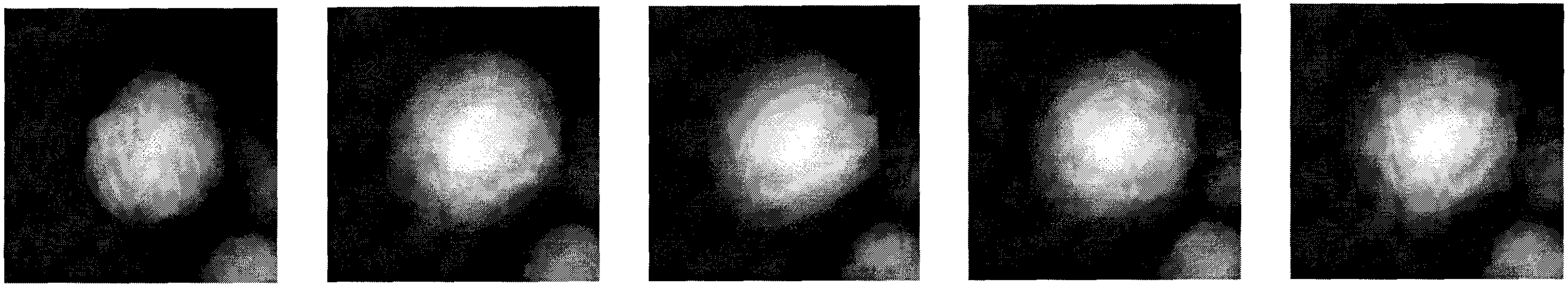
Spherical, crystalline nanoparticle layers with tight size control and good areal coverage have been obtained

Particle manipulation with an AFM

- *Image in tapping mode*
- *Manipulate in contact mode*

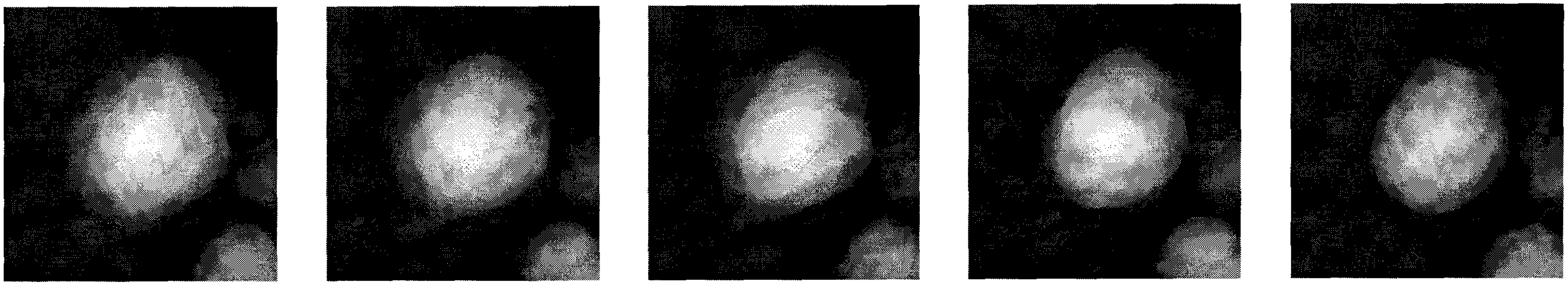


Individual Nanocrystal Charging/Discharging



Before charging

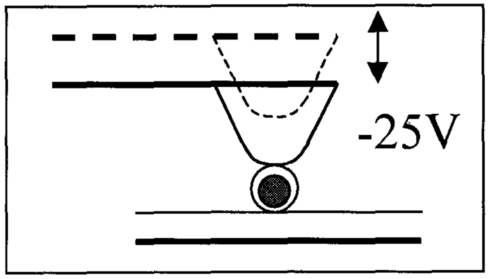
After charging
T=0s



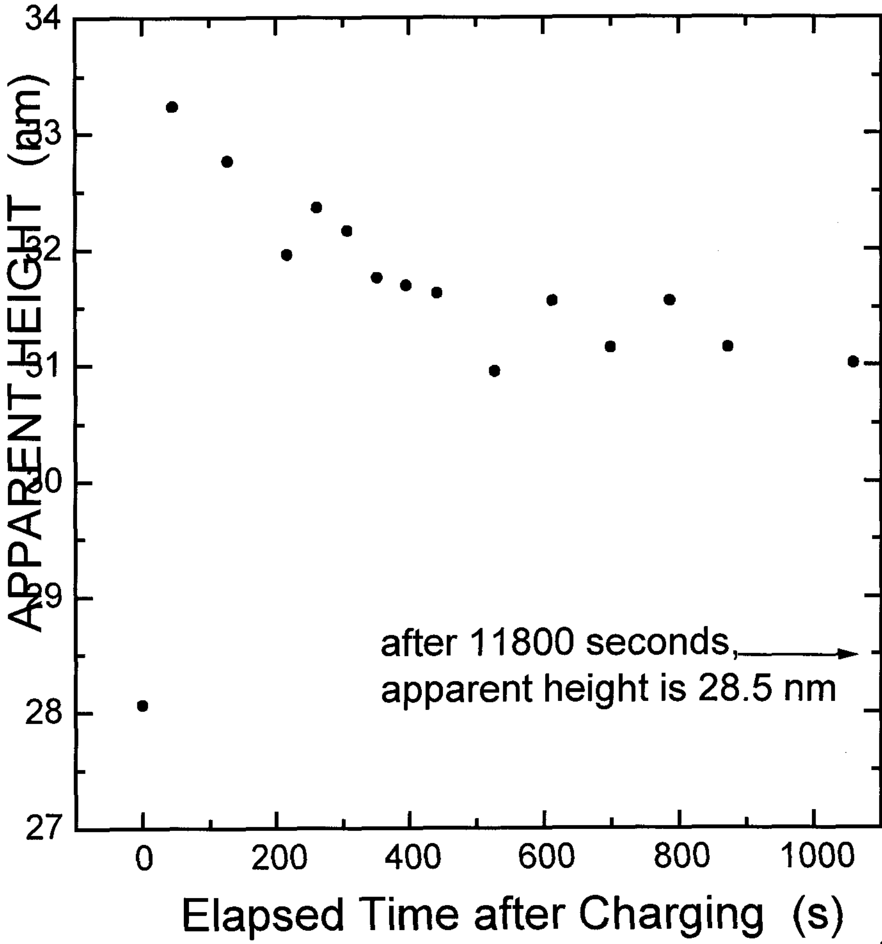
After charging
T=11800s

Charge storage in *individual* nanocrystals has been observed

Nanocrystal Charging/Discharging by AFM



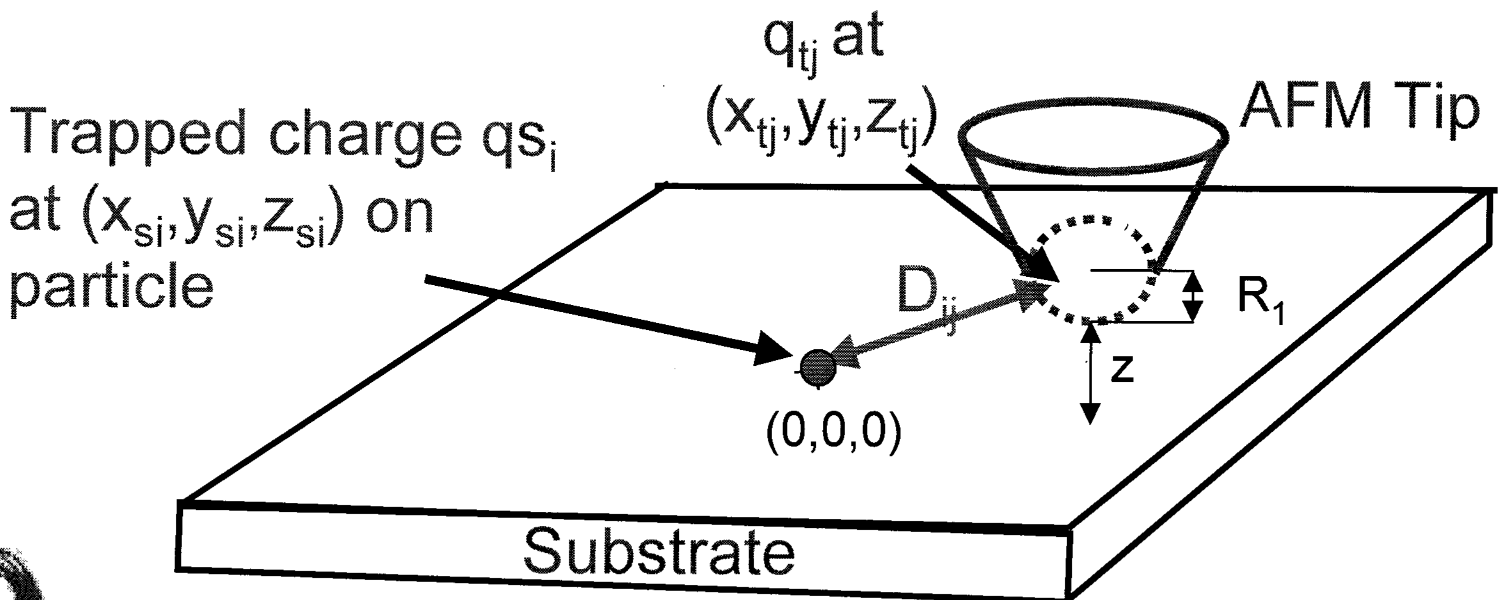
- Apparent height measured by AFM changes as Particle charges and discharges.
- Electron storage in a *single nanocrystal* can be monitored.



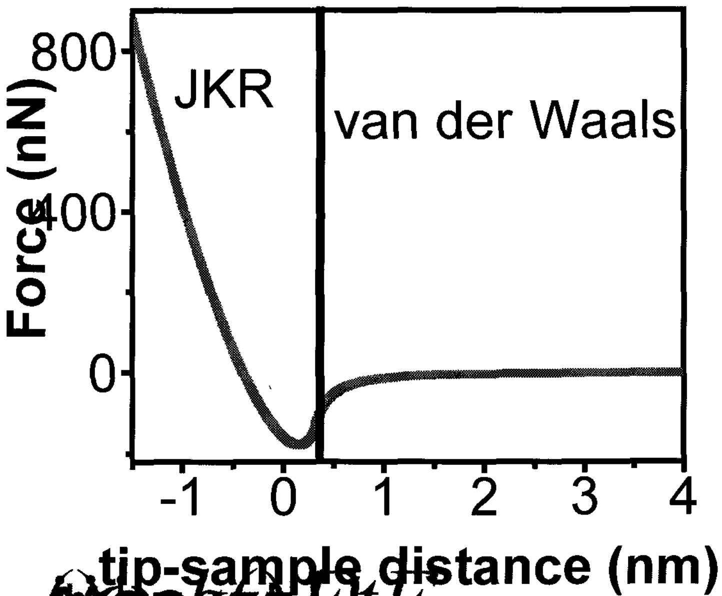
AFM Tip-Charge Distribution Interaction

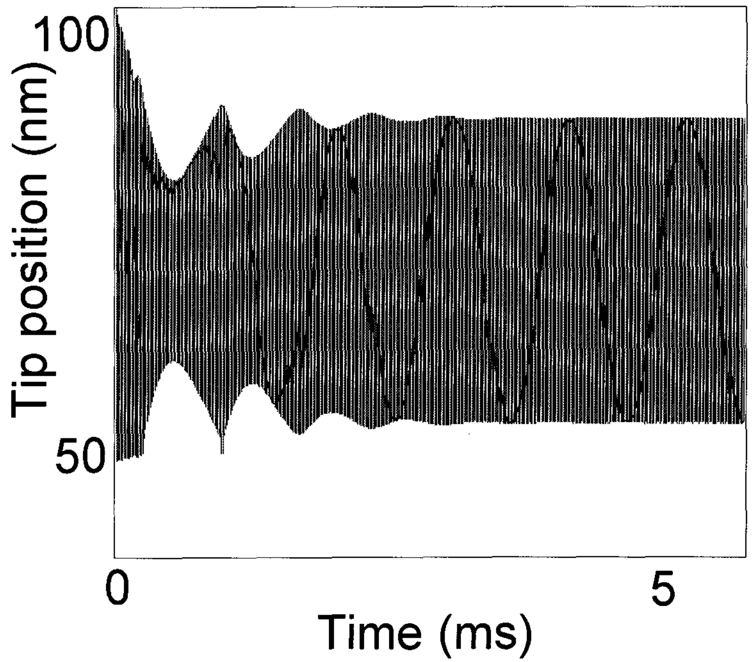
(aerosol samples)

Now include topography (single particle)

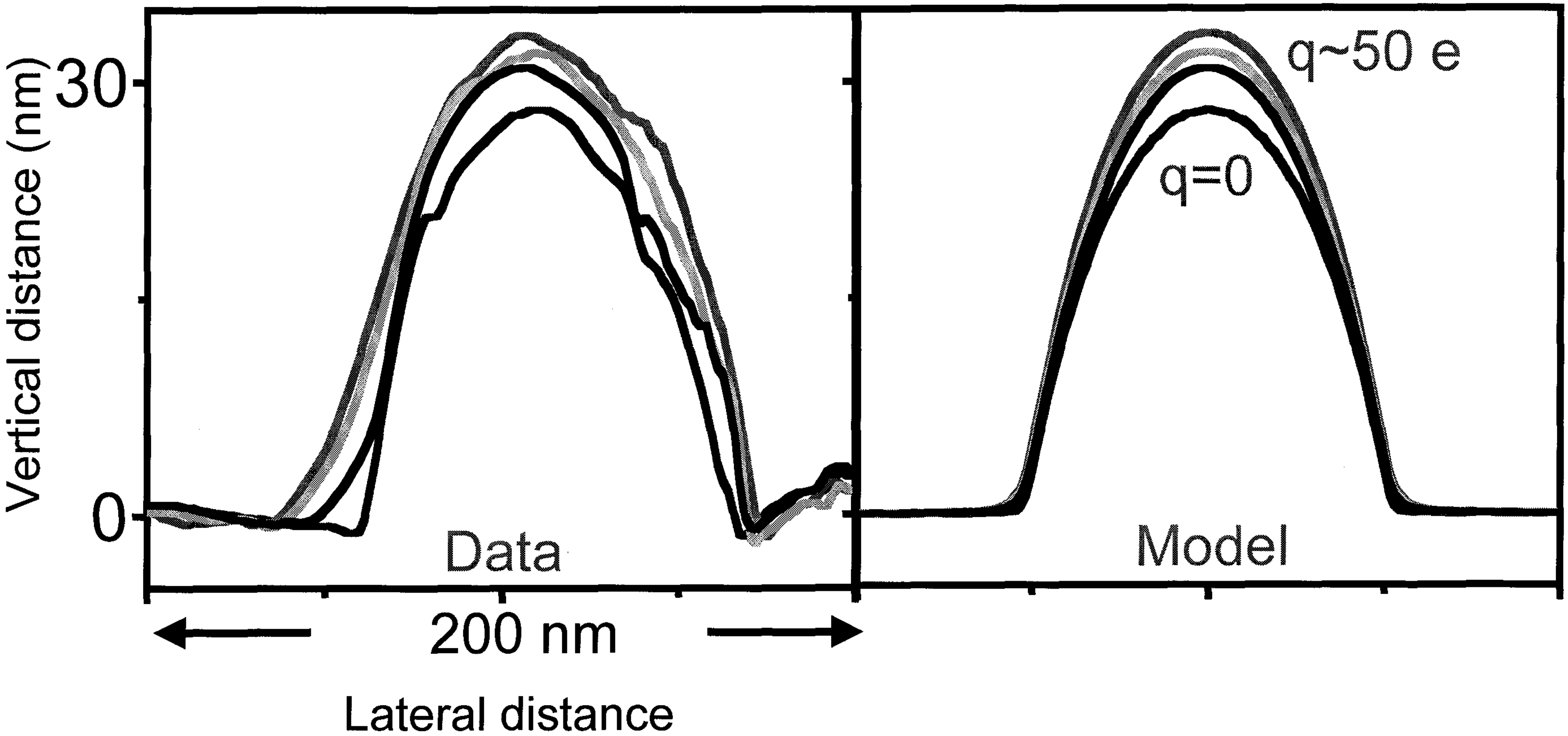


AFM Tapping-Mode Modeling



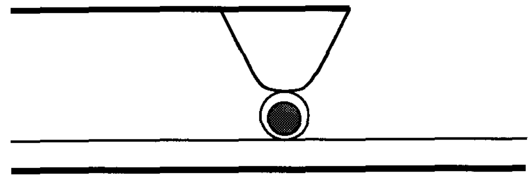


Comparison: Data and Model

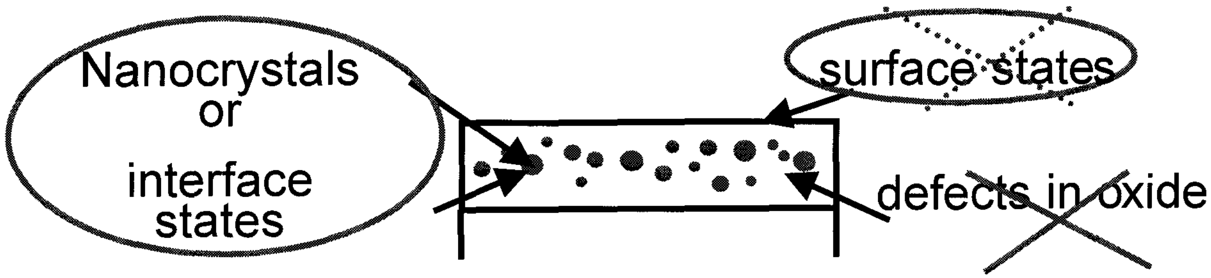


Model can reproduce the nanocrystal discharging behavior and yields the amount of ***charge stored****.*

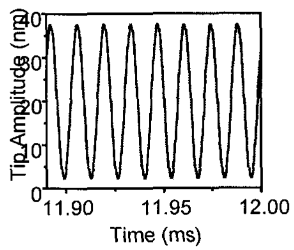
AFM Charging of Nanocrystals: Summary



- An AFM may be used to manipulate and charge size-controlled Si nanocrystals

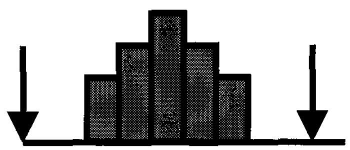


- Charge traps in films containing nanocrystals are not bulk oxide defects



- Average charge density deposited can be found from modeling

- The main discharge path appears to be to the substrate



Conclusions

- Si Nanocrystal charging has been accomplished with a conducting-tip AFM
- Both individual nanocrystals on an oxide surface and nanocrystals formed by implantation have been charged.
- Discharging is consistent with tunneling through a field-lowered oxide barrier
- Modeling of the response of the AFM to trapped charge has allowed estimation of the quantity of trapped charge.
- Initial attempts to fabricate competitive nanocrystal non-volatile memories have been extremely successful.